

REMARKS/ARGUMENTS

Favorable reconsideration of this application as presently amended and in light of the following discussion is respectfully requested.

Claims 1-8 and 25-29 are presently active. Claims 9-24 have been canceled without prejudice or disclaimer. Claims 1, 6 and 8 have been presently amended. Claims 25-29 have been added. No new matter has been added.¹

In the outstanding Office Action, Claims 1 and 4-7 are rejected under 35 U.S.C. § 102(b) as being anticipated by Zanini-Fisher et al (U.S. Pat. No. 5,451,371). Claims 2 and 3 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Zanini-Fisher et al in view of Elbel et al (U.S. Pat. No. 4,665,276).

Claim Summary: Claim 1 as clarified defines:

A micro thermoelectric gas sensor comprising:

a membrane for heat shielding formed on a substrate;

a catalyst material that induces a catalytic reaction in contact with a gas to be detected;

a thermoelectric conversion material film that converts a local temperature difference produced by heat generation caused by the reaction into a voltage signal;

a microheater for temperature control for facilitating stable gas detection of the gas sensor formed, which are on the membrane; and

a high-temperature section and a low-temperature section of a thermoelectric thin film formed on the same membrane. [Emphasis added]

Thus, Claim 1 defines a thermoelectric conversion material film having a high-temperature section and a low-temperature section formed on the same membrane. As described in Applicants' background section, in order to ensure stable operation of a gas sensor, the gas sensor has to be heated to a high temperature. The conventional heaters

¹ Support for the changes to Claim 1 is self-evident from original Claim 1. Support for the new claims is found in Applicants' Figures 1 and 3 and in the specification pages 11-19.

designed for this purpose have been formed by printing, e.g., a platinum resistor in the form of a thick film with a thickness of several tens of microns on a ceramic substrate. Such sensor elements are difficult to miniaturize. Yet another problem is that, because the entire ceramic substrate is heated, the sensor has a poor response of several minutes to temperature increase and a high power consumption of several watts. See Applicants' specification, page 2.

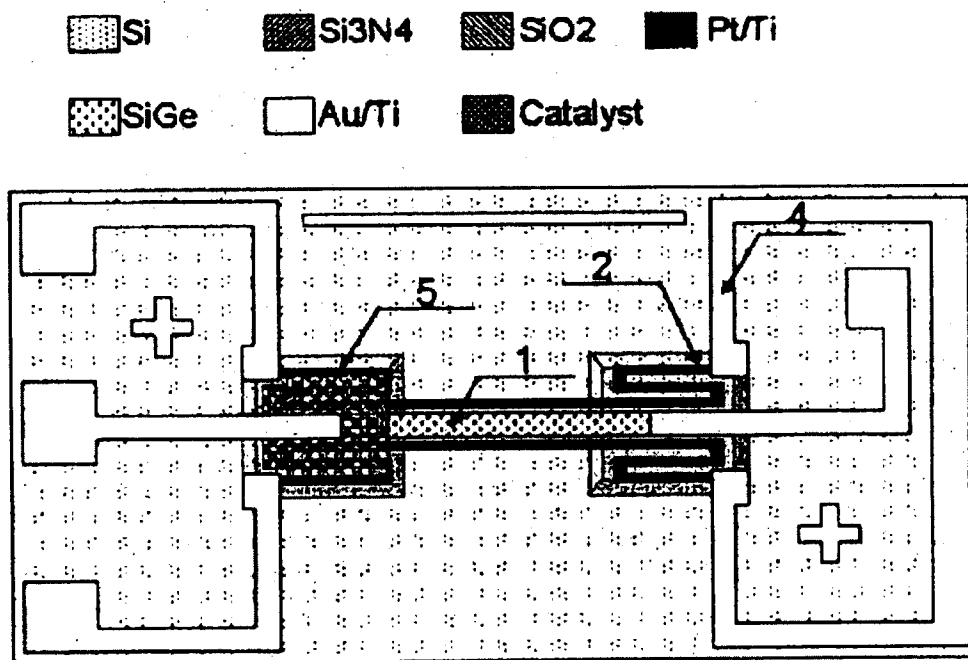
With these and other problems in mind, the inventors have conducted a comprehensive study aimed at the development of a novel technology that can solve the problems inherent to the conventional technology and produce a microelement structure of a thermoelectric gas sensors. The results obtained have demonstrated that a gas sensor element that has a low power consumption and a high-speed response and is suitable for concentration measurements with high sensitivity can be realized by forming a high-temperature section and a low-temperature section of a thermoelectric thin film on the same substrate. See Applicants' specification, page 11.

Applicants' Figure 1 shows such a construction where a silicon substrate 6 having appropriate insulators and thermoelectric materials deposited thereon has been etched to create membrane 8 on which the catalyst 5, the thermoelectric conversion material 1, and the electrodes 4 are formed along with the heater elements 2 on the same membrane. Applicants' Figure 3 shows a more detailed top down view of this configuration where the resistance heater element 2 patterned in a serpentine strip is located on one side of the membrane and the catalyst material 5 is located on another side of the membrane with a thin strip of thermoelectric material connecting therebetween.

Figure 3 is reproduced below for the sake of convenience, and shows one specific example of a SiGe thermoelectric material, which in this example extends from the high-temperature section (nearby the catalyst material 5) to the low-temperature section (nearby

heater element 2). Any difference in heat generated by reaction of gas with the catalyst material 5 generates a voltage due to a temperature difference across the thermoelectric conversion material 1. See specification, page 12, lines 17-23.

Applicants' Figure 3



Art Deficiencies: The Zanini-Fisher et al reference was applied in the Office Action for anticipating the elements in Claim 1. However, the Office Action apparently associates temperature sensing conductors 64 in Figure 2C of Zanini-Fisher et al with the claimed thermoelectric conversion material film. Yet, as described in Zanini-Fisher et al, element 64 is a portion of resistor 62, and “resistors 46 and 62 serve as thermometers.” See col. 4, lines 27-43 of Zanini-Fisher et al. The description in Zanini-Fisher et al of a resistor is **not** a disclosure or suggestion of a thermoelectric conversion material film. For the examiner’s

appreciation, attached herewith is a 1999 paper entitled “Thermoelectric Materials” which shows that a thermoelectric material is one where a voltage develops across the material due to a temperature differential across the material. In the resistors of Zanini-Fisher et al, one applies a voltage, measures a current, and computes the resistance. The resistance is known as a function of temperature, and the measured resistance compared to this known functional dependence in order for the resistors of Zanini-Fisher et al to serve as thermometers.

Furthermore, the function of the polysilicon material in Zanini-Fisher et al (see col. 4, lines 26-37) is as a “pellistor” (described in more detail in the background section of Zanini-Fisher et al). The function of the polysilicon material in Zanini-Fisher et al is **not** that of a thermoelectric (Seebeck effect) conversion material. The origin of the word “pellistor” is that a pellistor sensor consists of a small heating element coated by “pellets” of catalyst loaded ceramic, which burns a gas, and heat induces the changes of the resistance of the “resistor” element. The most famous report on the technology of pellistor sensors using micro-device process is the reference of Gall et al (1991), which is described in the reference of Zanini-Fisher et al.

Micro pellistor sensors have been obtained from depositing of the catalytic materials on silicon micromachined substrates (micro-hotplates), as these devices have been fabricated on silicon substrate and Si_3N_4 has been used as dielectric membrane. The resistor heaters were typically made of poly-silicon or Pt metal resistor.

Thus, a pellistor as used in Zanini-Fisher et al is a kind of calorimetric sensor, which uses the change of the resistance, to sense changes in “absolute temperature.” The use of polysilicon or SiGe pellistor does not disclose or suggest the claimed thermoelectric conversion material film that converts a local temperature difference produced by heat generation caused by the reaction into a voltage signal.

The deficiencies in Zanini-Fisher et al are not overcome by Elbel et al. Elbel et al, in Claim 1, describes their device structure as “said two legs contacting each other in a reference junction over said substrate,” which means that a cold or low temperature section contacts on the substrate (not on the membrane). Elbel et al, in Claim 1, describes their device structure as “each of said contacting one leg of its neighboring thermocouple in sensing junction above said aperture,” which means that the hot temperature sections are on the membrane (or aperture), which is typical structure of thermopile device. Thus, Elbel et al in disclosing the placement of thermocouple junctions likewise do not disclose or suggest thermoelectric conversion material film that converts a local temperature difference produced by heat generation caused by the reaction into a voltage signal, and furthermore does not disclose or suggest a high-temperature section and a low-temperature section of a thermoelectric thin film formed on the same membrane, as claimed.

Indeed, it is the inventors alone that have demonstrated the extremely high sensitivity of their thermoelectric sensor, which can detect sub ppm level hydrogen while the detection limit of the pellistor type sensors are around 500 ppm level hydrogen.

By adopting the specific constitution wherein a high-temperature section and a low-temperature section of the thermoelectric thin film are formed on the same membrane, the extremely high sensitivity capability of the thermoelectric sensor detecting sub ppm level hydrogen has been accomplished for the first time by the inventors.

Indeed, without the knowledge from Applicants' specification, one of ordinary skill in the art would have no motivation or otherwise no rationale to modify either of the Zanini-Fisher et al or the Elbel et al structures to produce the claimed invention wherein a high-temperature section and a low-temperature section of the thermoelectric thin film are formed on the same membrane.

M.P.E.P. § 2131 requires for anticipation that each and every feature of the claimed invention must be shown in as complete detail as is contained in the claim. M.P.E.P. 2141 II indicates that, in short, the focus when making a determination of obviousness should be on what a person of ordinary skill in the pertinent art would have known at the time of the invention, and *on what such a person would have reasonably expected to have been able to do in view of that knowledge.*

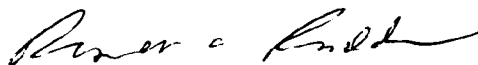
Thus, without Zanini-Fisher et al and Elbel et al individually or in combination providing the details of the claimed micro thermoelectric gas sensor and without a person of ordinary skill in the art at the time of the invention knowing of the advantages discovered by the inventors, Claim 1 when considered as a whole patentably defines over Zanini-Fisher et al and Elbel et al. Hence, Claim 1 and the claims depending therefrom are believed to contain allowable subject matter and should be passed to allowance.

New Claims: Claims 25-27 have been added reciting features shown in Applicants' Figures 1 and 3. These claims set forth features not disclosed or suggested in Zanini-Fisher et al or Elbel et al and set forth features consistent with Applicants' utilization of a thermoelectric conversion material film, rather than a resistance element. Hence, these claims (besides their dependence from allowable Claim 1) define separately patentable subject matter.

Conclusion: In view of the present amendment and in light of the above discussions, the outstanding grounds for rejection are believed to have been overcome. The application as amended herewith is believed to be in condition for formal allowance. An early and favorable action to that effect is respectfully requested.

Respectfully submitted,

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Thermoelectric Materials

ABSTRACT

When a thermal gradient is applied to a solid, it will be accompanied by an electric field in the opposite direction; this is known as the thermoelectric effect. The physics principles that are used to explain this phenomenon and how these principles relate to the research of materials that exhibit the largest thermoelectric effect will be reviewed. Thermoelectric material applications include refrigeration or electrical power generation. Current state of the art materials and research being done to find better materials will be discussed. Theoretically, there is no limit to the thermoelectric effect, and a substantial research effort is currently underway.

INTRODUCTION

Thomas Seebeck discovered the thermoelectric effect in materials in 1823 when he noticed that a voltage drop occurs across a material with a temperature gradient. However, like many other discoveries, it took many years to find useful applications and materials for this discovery. In the 1950s, Abraham Ioffe showed that doped semiconductors showed a much larger thermoelectric effect than other materials. This led to research of binary semiconductors as thermoelectric materials in the 1950s, with Bi_2Te_3 having the greatest thermoelectric effect at room temperature. The research led a good understanding of the properties displayed by a good thermoelectric material. It was not until the 1990s that interest increased again due to new materials discoveries with the potential for excellent thermoelectric properties.

PHYSICS PRINCIPLES FOR THE THERMOELECTRIC EFFECT, AND THE FIGURE OF MERIT, Z

When a thermal gradient is applied to a solid, it will be accompanied by an electric field in the opposite direction; this is known as the thermoelectric effect, and was discovered by Thomas Seebeck in 1826. It is easiest to show this effect using a one-dimensional model. A thermal gradient is applied along a line taking point x to be halfway between the low and high temperature sides. The electrical field, E , generated from a thermal gradient can be conveniently written as

$$E = Q \nabla T$$



where v is the electron velocity, and τ is the relaxation time. $x-v\tau$ represents the position of the last electron collision on the high temperature side of x , and $x+v\tau$ represents the position on the low temperature side. To convert to the three dimensional case, consider $v=v_x$, and assume that the electron velocities are equivalent in three dimensions, i.e. $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = 1/3 \langle v^2 \rangle$, so that

$$v_Q = -\frac{\tau}{6} \frac{d v^2}{dT} (\nabla T)$$

The mean velocity, v_E , due to the electric field, E is

$$v_E = eE\tau/m$$

where e is the electron charge and m the electron mass. The mean thermal and electronic velocities are equal and are travelling in opposite direction, so $v_Q = -v_E$. Solving for Q we get

$$Q = -\left(\frac{1}{3e}\right) \frac{d}{dT} \frac{mv^2}{2} = -\frac{c_v}{3ne}$$

where c_v is the heat capacity for free electrons

$$c_v = \frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) nk_B$$

substituting c_v into the equation for the Seebeck Coefficient, Q we get

$$Q = -\frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{\epsilon_F} \right) = -1.42 \left(\frac{k_B T}{\epsilon_F} \right) \times 10^{-4} \text{ volt/K}$$

A material's Seebeck Coefficient, Q , electrical conductivity, σ , and thermal conductivity, κ , all relate to the efficiency of a thermoelectric material by the figure of merit, Z

$$Z = Q^2 \sigma / \kappa$$

where Z is in unit $(1/^\circ\text{K})$. A more useful method of describing the thermoelectric efficiency of a material system is by using the dimensionless figure of merit, ZT , where T is the temperature of interest. The dimensionless figure of merit, ZT will be used throughout the paper to compare the efficiencies of different material systems.^{1,2}

APPLICATIONS

One of the two main applications of thermoelectrics is for refrigeration purposes, and is called Peltier refrigerators. An electrical current applied across a material will cause a temperature differential, which can be used for cooling. Bi_2Te_3 is the thermoelectric material of choice for this application, $ZT=0.9$ at room temperature. Bi_2Te_3 materials cannot meet the efficiencies to compete with compressor based refrigeration systems, which is equivalent to $ZT=3$. Peltier thermoelectrics are more reliable than compressor based refrigerators, and are used in situations where reliability is critical. NASA uses thermoelectric materials to cool down

power. The principle would be to use exhaust heat generated by another application such as an automobile engine, and create electrical power.¹

MATERIAL PROPERTIES

To maximize the dimensionless figure of merit, ZT , the Seebeck coefficient and electrical conductivity are maximized, while simultaneously minimizing the thermal conductivity. The best thermoelectric materials will have a small electronic contribution to the thermal conductivity, κ_e , thus maximizing the electronic conductivity while minimizing the thermal conductivity. The Weidmann-Franz law states that

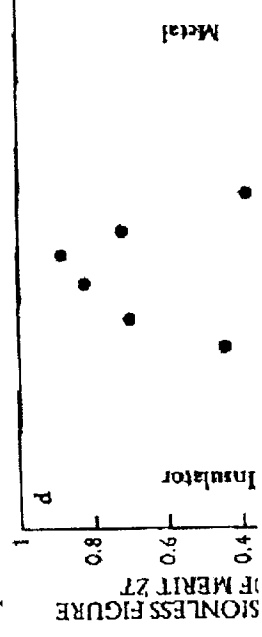
$$\kappa_e/\sigma T = L_0 = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$$

Therefore the electronic contribution of the thermal conductivity is a constant (Lorenz number= L_0) at a given temperature. The total thermal conductivity, is the sum of the electronic and lattice contributions $\kappa = \kappa_e + \kappa_{\text{lat}}$. Finding materials that minimize the lattice contribution to the thermal conductivity will maximize the dimensionless figure of merit.

Metals are poor thermoelectric materials because they have a low Seebeck coefficient, and large electronic contribution to thermal conductivity, so σ and κ will cancel each other out. Insulators have a high Seebeck coefficient, and a small electronic contribution to thermal conductivity, however their charge density and therefore electrical conductivity are low leading to a low thermoelectric effect. The best thermoelectric materials are between metals and insulators; i.e. semiconductors with an electronic density of $10^{19}/\text{cm}^3$, see Figure 1.

The next step is finding semiconductors with a low lattice contribution to the thermal conductivity, thus maximizing the dimensionless figure of merit. The materials with the lowest κ_{lat} have large a large number of atoms in the unit cell, a large average atomic mass, and a large average coordination number per atom thus lowering the mean free path. Another method of reducing κ_{lat} is finding a unit cell with cages, or voids, with loosely bound atoms that can "rattle" and thus scatter phonons.

There are four groups of materials that are being researched. Normal broadband semiconductors, semiconductors with rattling atoms or molecules, "correlated" metals or superconductors, and superlattices, also called multiple quantum well materials.¹



NORMAL BROADBAND SEMICONDUCTORS

There already has been a substantial effort in finding p-type or n-type binary semiconductors with high dimensionless figures of merit. The current state of the art materials include Bi_2Te_3 ; $ZT=0.9$ at room temperature, PbTe ; $ZT=1.2$ at 700°K , and SiGe ; $ZT=0.6$ at 1000°K .

Large values of electronic conductivity are necessary for good thermoelectric materials; thus large values of electron or hole mobility are needed. It can be shown that maximizing ZT is equivalent to maximizing U/κ_{lat} , where U is the weighted mobility for electrons and holes

$$U = N\mu m^{*3/2}$$

N is the number of equivalent parabolic bands, μ is the electron or hole mobility, and m^* is the effective mass. Covalently bonded semiconductors will have the highest effective mobility. To maximize ZT , we need superconductors with $U > 0.02 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, and $\kappa_{\text{lat}} < 3 \text{ W m}^{-1} \text{K}^{-1}$, see Figure 2. These quantities are a good starting point to determine the thermoelectric efficiency of semiconductor materials. Research is focused towards finding ternary materials that maximize ZT .^{1,3}

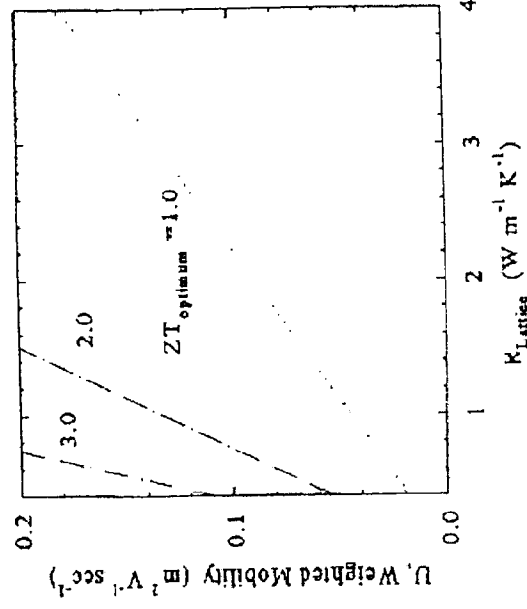


Figure 2 – Lines of Constant ZT in the Weighted Mobility versus κ_{Lattice}

“RATTLING” SEMICONDUCTORS

The main approach to reducing the lattice contribution of the thermal conductivity has been to lower the mean free path by using heavy atoms within large unit cells. However, the

group of the periodic table. To form the loosely bound void, the R atom radius has to be smaller than the void radius of the unit cell. Nolas and Slack proved this principle by adding La – 1.79Å, Nd – 1.70Å, and Sm 1.69Å to the IrSb₃ binary (not filled) skutterudite unit cell with a void radius of 2.04Å. An order of magnitude decrease in the κ_{lat} was exhibited by filling the cages in the binary skutterudite crystals.⁴ This effect is also shown in Figure 4 by adding La or Ce to the CoSb₃ binary skutterudite crystals to form RFe₃CoSb₁₂ where R represents La or Ce. The best dimensionless figure of merit at room temperature is only $ZT=0.25$, but these structures show great promise at higher temperatures.^{1,4}

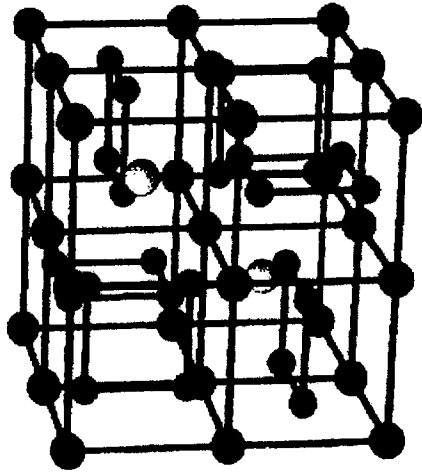


Figure 3 – Filled Skutterudite Crystal

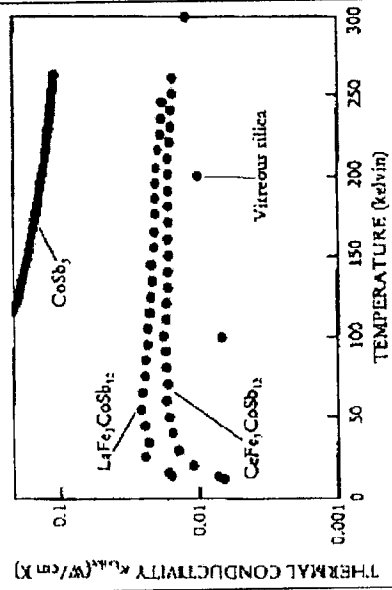


Figure 4 – $\kappa_{Lattice}$ versus Temperature for LaFe₃CoSb₁₂, CeFe₃CoSb₁₂ and CoSb₃

CORRELATED METALS AND SEMICONDUCTORS

Correlated metals and semiconductors, or Kondo insulators are described by rare earth intermetallic compounds usually containing Ce. Metals are not good thermoelectric materials due to a low Seebeck coefficient; however, this is not true for rare earth intermetallic compound where the 4f level is close to the fermi energy. These compounds have a high density of states near the fermi energy, thus scattering conduction electrons. A simple power law no longer describes the scattering time, but now exhibits resonant scattering. The Kondo effect, which relates to the scattering of conduction electrons, shows compounds with large Seebeck coefficients at low temperatures, reference Figure 5. Compounds such as CePd₃ show Q as high as 115 $\mu V/^{\circ}K$ at low temperature. It should be noted that Q or S could represent the Seebeck coefficient interchangeably. The minimum value of Q, when $\kappa_{lat}=0$, has to be $Q=156 \mu V/^{\circ}K$ to have the dimensionless figure of merit, $ZT=1$. The best materials to date have only achieved dimensionless figure of merit $ZT=0.75$ at below 1.5

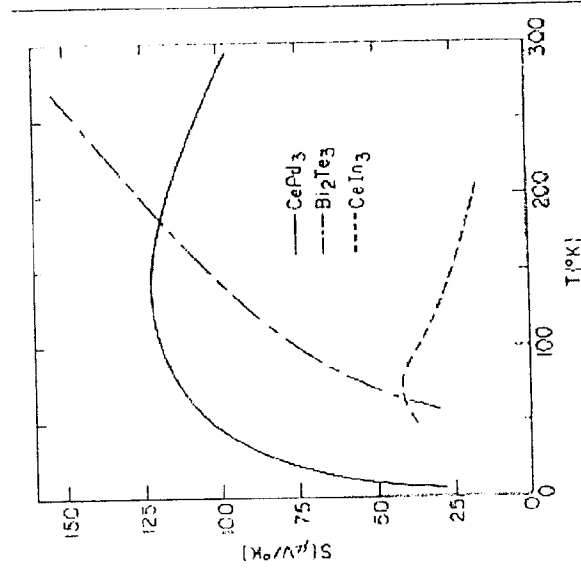


Figure 5 - Seebeck Coefficient versus temperature for CePd₃, CeIn₃, and Bi₂Te₃

SUPERLATTICES

Superlattices or Multiple Quantum Well (MQW) structures are materials that will only conduct electrons in two dimensions, thus increasing the density of states with decreasing well widths. The increase in density of states will increase a materials figure of merit, by increasing the $Q^2\sigma$ factor, assuming no change in the thermal conductivity. It is also assumed that there is no change between the electron mobility of the bulk material, and the quantum well, so any increase in Z would arise through the factor Q^2n , where n is the electron density. Values of Q^2n versus well thickness are shown in Figure 6, and give good agreement between experiment and theory. Lowering the well thickness, and using multiple quantum well structures shows a large increase in Q^2n , and thus Z . Thomas Reinke at Naval Research Laboratories has shown a 20% improvement in the ZT of multiple quantum well structures versus bulk material. At quantum wells $\leq 10\text{\AA}$, phonons will be scattered by the interfaces between quantum wells, thus lowering the thermal conductivity, and further enhancing the KT value. The theory neglects two physical effects that will lower the dimensionless figure of merit. Thermal current flows through the quantum wells and the barrier layer equivalently, thus lowering the electrical conductivity in the quantum wells. In addition, electron tunneling will occur between quantum wells, which lowers the systems density of states, thus lowering the ZT value. Theoretically, the largest values for the dimensionless figure of merit can be reached using this method 1.6,7,8

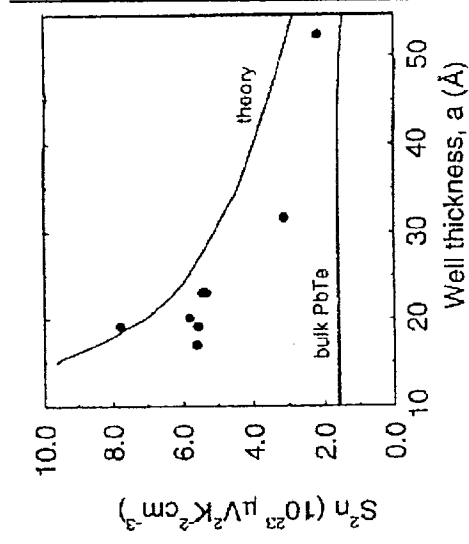


Figure 6 - $Q^2 n$ versus Well Thickness for Multiple Quantum Well PbTe. The black dots represent experimental data points for PbTe.

CONCLUSIONS

The potential uses of thermoelectric materials as Peltier refrigerators, or for power generation are limitless if the dimensionless figure of merit, ZT can reach a value of 3 or larger. There are currently a few applications in practice that require high reliability, most notably NASA's use of thermoelectric materials to cool deep space probes to temperatures as low as 160°K. There are four groups of materials that are being researched. Normal broadband semiconductors, semiconductors with rattling atoms or molecules, "correlated" metals or superconductors, and superlattices, also called multiple quantum well materials. Semiconductors with "rattling" atoms, and multiple quantum wells have the greatest potential for improving the ZT value, and improved values of ZT have already been shown experimentally.

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